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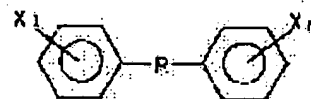
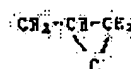
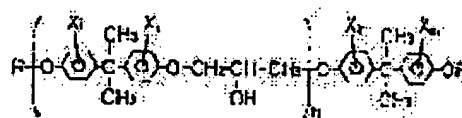
(54) FLAME-RETARDANT STYRENIC RESIN COMPOSITION

(57)Abstract:

PURPOSE: To obtain a flame-retardant styrenic resin compsn.

excellent in flame retardance and the balance among heat resistance, impact resistance, and flowability by compounding a styrenic resin with two specific halogenous flame retardants, an auxiliary flame retardant, and a small amt. of polytetrafluoroethylene.

CONSTITUTION: This resin compsn. comprises 100 pts.wt. styrenic resin (A), 2-18 pts.wt. halogenated arom. -diol-based ether deriv. (B) having a wt.-average mol.wt. of 500-10,000 [a compd. of formula I (wherein R is H, a group of formula II, etc.; X is Br or Cl; (i), (j), (k), and (m) are each 1-4; and (n) is 0-30)], 2-16 pts.wt. polyhalogenated diphenylalkane (C) of formula III [wherein X is Br or Cl; (l) and (m) are each 0-5 excluding the case where they are both 0; and R is C_nH_{2n} (wherein (n) is 1-10)], 1-10 pts.wt. Sb₂O₃ (D), and 0.01-0.5 pt.wt. polytetrafluoroethylene (E), the sum of components B and C being 12-21 pts.wt. Thus, a compsn. excellent in flame retardance and the balance among heat resistance, impact resistance, and flowability is obtd. with a reduced amt. of halogenous flame retardants.



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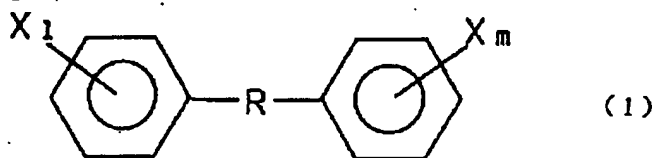
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CLAIMS

[Claim(s)]

[Claim 1] (A) The fire-resistant styrene-resin constituent which consists of 2 - 16 weight section, the (D) antimony trioxide 1 - 10 weight sections, and the (E) polytetrafluoroethylene 0.01 - the 0.5 weight sections the poly halogenation diphenyl alkane shown by the styrene-resin 100 weight section, the ether derivative 2 of the halogen content aromatic diol of the (B) weight average molecular weight 500-10000 - 18 weight sections, and (C) following (1) formula, and is characterized by (B)+(C) being 12 - 21 weight

[Formula 1]



[-- X shows a bromine atom or a chlorine atom among a formula, l and m show the integer (however, not both bird clappers have l and m in 0.) of 0-5, and R shows $C_n H_{2n}$ ($n=1-10$)]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to thermal resistance, shock resistance, and the styrene-resin constituent excellent in fluid balance while it is excellent in fire retardancy in detail about a styrene-resin constituent.

[0002]

[Description of the Prior Art] The styrene resin is used over the reason of the outstanding fabricating-operation nature, a mechanical characteristic, and an electrical property in many fields. However, since it is a flammability, flameproofing of a resin is needed in case it is used for parts housing of OA equipment and home electronics and the electrical and electric equipment, and electronic-related etc. It is regulated by UL etc. about this fire retardancy, and the means of flameproofing various in recent years is examined. In the housing field of home electronics, the above-mentioned flameproofing regulation and thermal resistance, shock resistance, and a fluidity are searched for into it, and the styrene resin which maintained the balance which fills all these military requirements is called for.

[0003] Generally, using together and using a high-melting point type halogen system flame retarder and antimony trioxides, such as deca BUOMO diphenyloxide, as flameproofing of a styrene resin is shown in JP,58-187450,A. However, there was a problem of a fluid fall and degradation of the lightfastness of mold goods as a fault of this flame retarder. Furthermore, the toxicity of the gas which occurs at the time of the conditions which have this flame retarder in recent years is taken up as an environmental problem.

[0004] Moreover, using together and using a bromination bisphenol A type epoxy resin and an antimony trioxide is shown in JP,63-72749,A. However, this flame retarder had a problem also in cost, in the fire-resistant dose of a considerable amount is needed, therefore shock resistance and thermal resistance falling remarkably, in order to acquire the target fire retardancy, since halogen content is low.

[0005] Moreover, if flameproofing of the poly halogenation diphenyl alkane is used and carried out to a styrene resin, in order to obtain the fire-resistant performance made into the purpose, the solid-state of an unmelting system will be added to a resin so much, and there was a problem that an impact strength and a fluidity fell. Moreover, although using together and using a poly halogenation diphenyl alkane and a bromination bisphenol A type epoxy resin was shown in JP,6-73268,A, it was very difficult for there to be problems, such as a fluid fall by adding a poly halogenation diphenyl alkane and a fall of the shock nature by adding a bromination bisphenol A type epoxy resin, and to maintain balance.

[0006] On the other hand, many researches are made about the addition to the resin of a halogen inclusion and a polytetrafluoroethylene. For example, JP,59-36657,B, JP,60-13844,A, JP,62-58629,B, JP,64-3900,B, JP,2-32154,A, Although there is JP,5-27531,A etc., a basic resin [all] is the combined use system of a polycarbonate oligomer system and an acrylonitrile-styrene-butadiene-rubber system, or a denaturation polyphenylene-ether system. And addition of a polytetrafluoroethylene is the purpose which decreases the melting dropping nature which those resins have. Moreover, although JP,50-44241,A had the publication about the polystyrene system, there was a problem that the effects differed greatly, according to the kind of halogenide to add.

[0007]

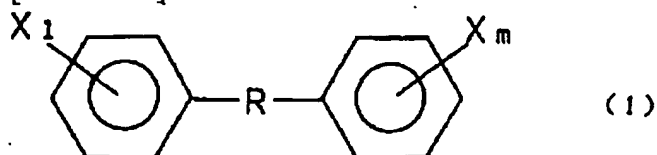
[Problem(s) to be Solved by the Invention] this invention aims at offering thermal resistance, shock resistance, and the styrene-resin constituent excellent in fluid balance while it is excellent in fire retardancy. [0008]

[Means for Solving the Problem] Then, this invention persons decrease the addition of a specific halogen system flame retarder by blending with a styrene resin combining two sorts of halogen system flame retarders, a specific fire-resistant assistant, and a specific little polytetrafluoroethylene, as a result of repeating research wholeheartedly that the above-mentioned technical problem should be solved, and it finds out attaining the purpose and comes to complete this invention.

[0009] this invention Namely, the (A) styrene-resin 100 weight section, the ether derivative 2 of the halogen content aromatic diol of the (B) weight average molecular weight 500-10000 - 18 weight sections, (C) The poly halogenation diphenyl alkane shown by following the (1) formula 2 - 16 weight section, (D) It consists of an antimony trioxide 1 - the 10 weight sections, and the (E) polytetrafluoroethylene 0.01 - 0.5 section, and the fire-resistant styrene-resin constituent characterized by (B)+ (C) being 12 - 21 weight section is offered.

[0010]

[Formula 2]



[0011] [-- X shows a bromine atom or a chlorine atom among a formula, l and m show the integer (however, not both bird clappers have l and m in 0.) of 0-5, and R shows C_nH_{2n} ($n=1-10$)] this invention is explained in detail below. The styrene resin (A) used by this invention says the polymer which a rubber-like polymer comes to distribute in the shape of a particle into the matrix which consists of a vinyl aromatic polymer, generally a rubber-like polymer is dissolved in a vinyl aromatic monomer (and liquid which added the inert solvent), and a bulk polymerization, a massive suspension polymerization, or solution polymerization is performed under churning, and although obtained by depositing and particle-izing a rubber-like polymer, it is not limited to a polymerization method.

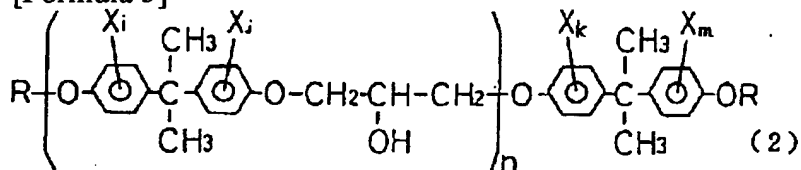
[0012] As the above-mentioned vinyl aromatic monomer, although alpha-alkylation styrene, such as nucleus alkylation styrene, such as o-methyl styrene besides styrene, p-methyl styrene, m-methyl styrene, 2, 4-dimethyl styrene, ethyl styrene, and p-tertiary-butyl styrene, an alpha methyl styrene, and an alpha-methyl-p-methyl styrene, etc. can be mentioned, a typical object is styrene. These may use together the two or more sorts.

[0013] Moreover, as the aforementioned rubber-like polymer, although a polybutadiene, a styrene butadiene copolymer, a polyisoprene, a butadiene isoprene copolymer, natural rubber, and an ethylene propylene rubber can be mentioned, generally a polybutadiene and a styrene butadiene copolymer are desirable. The weight average molecular weight of the matrix portion of the rubber denaturation vinyl aromatic resin which constitutes the resin constituent of this invention is 15×10^4 from a strong relation. Usually is adjusted to the above range, and if less than this, intensity will fall rapidly.

[0014] Although there are especially no restrictions about the rubber-like polymer content of the above-mentioned rubber denaturation vinyl aromatic resin, generally it is 6 - 12 % of the weight more preferably four to 15% of the weight. Furthermore, the mean particle diameter of the rubber particle in the above-mentioned rubber denaturation vinyl aromatic resin is controlled by the range of 0.5-6.0 micrometers. Moreover, although the gel content (toluene insoluble) of the aforementioned styrene resin is adjusted to 15 - 40% of the weight of a conventional method, it is 20 - 35 % of the weight more preferably. Next, generally the ether derivative of a halogen content aromatic diol used by this invention is expressed with following the (2) formula.

[0015]

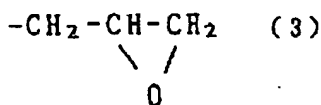
[Formula 3]

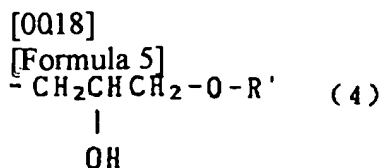


[0016] [-- R is expressed with a hydrogen atom, following the (3) formula, or following the (4) formula among a formula, in X, a bromine or a chlorine atom, and i, j, k and m show the integer of 1-4, and n shows the integer of 0-30]

[0017]

[Formula 4]





[0019] [R' shows a phenyl group (replaced by the low-grade alkyl group, the bromine, and/or the chlorine atom).] As an example, the resultant of ** halogen bisphenol A and a ** halogen bisphenol A epoxy resin, It is obtained by making ** halogen bisphenol A and epichlorohydrin react according to a conventional method. By changing the reaction ratio of ** halogen bisphenol A and a ** halogen bisphenol A epoxy resin It is also possible to also make to make an end into OH basis, to make it an epoxy group, or one side into OH basis, and to make another side into an epoxy group, and each resultant obtained by doing in this way gives suitable fire-resistant resin composition. The ether derivative obtained by making tribromophenol, pen tableau MOFE Norian, or a trichlorophenol react to an end epoxy group furthermore also serves as a flame retarder suitable for the purpose of this invention.

[0020] As an example of ** halogen bisphenol A, there are tetrabromobisphenol A, the dichlorobis phenol A, tetrapod chloro bisphenol A, a dibromobis phenol A, etc. Moreover, as an example of a ** halogen bisphenol A epoxy resin, there are diglycidyl ether of tetrabromobisphenol A, diglycidyl ether of tetrapod chloro bisphenol A, diglycidyl ether of the dichlorobis phenol A, diglycidyl ether of the dibromobis phenol A, etc.

[0021] It is the ether derivative especially reacted and obtained preferably in a resultant, and tetrabromobisphenol A and epichlorohydrin with the diglycidyl ether of tetrabromobisphenol A and tetrabromobisphenol A. Molecular weight of the flame retarder (B) expressed with the aforementioned (2) formula in this invention is made into weight average molecular weight, and needs to be 500-10000. Weight average molecular weight is inferior to 500 in a low, the thermal resistance of mold goods, and the thermal stability at the time of fabrication, and sufficient fire retardancy cannot be given. Moreover, when weight average molecular weight is higher than 10000, compatibility with a resin falls and shock resistance falls remarkably.

[0022] Next, the poly halogenation diphenyl alkane (C) in this invention is expressed with the aforementioned (1) formula. As an example of the phenyl group of halogenation, there are a dibromo phenyl, a TORIBUROMO phenyl, a tetrabromo phenyl, pentabromophenyl, dichlorophenyl, a TORIKURORO phenyl, tetrapod chlorophenyl, pentachlorophenyl, etc. Although especially the process of a flame retarder (C) is not limited, you may use what was manufactured by the method indicated by JP,2-42031,A or JP,6-73268,A, for example. Moreover, the Albemarle [the U.S.] bromination bibenzyl (tradename Saytex8010) is mentioned possible [also appropriating a commercial thing as a poly halogenation diphenyl alkane (C) used for this invention].

[0023] Furthermore, the antimony trioxide which is the (D) component of this invention is an object which acts as a fire-resistant assistant. For the ether derivative (B) of a halogen content aromatic diol, 2 - 18 weight section, the poly halogenation diphenyl alkane (C) 2 - 16 weight sections, and an antimony trioxide (D) are [1 - 10 weight section and a polytetrafluoroethylene (E)] the 0.01 - 0.5 weight sections, and (B)+ (C) of these blending ratio of coal to the styrene-resin (A) 100 weight section is 12 - 21 weight section. For 5 - 13 weight section and an antimony trioxide, 3 - 7 weight section and a polytetrafluoroethylene are [the ether derivative of a halogen content aromatic diol / 2 - 13 weight section and a poly halogenation diphenyl alkane / the 0.05 - 0.1 weight section and (B)+ (C)] 15 - 19 weight sections preferably.

[0024] When the manufacture method of the fire-resistant resin constituent of this invention carries out specified quantity combination of each of these components, especially the combination method does not have a limit and has the method of a Henschel mixer, a tumbler mixer, a super mixer, a Banbury mixer, a kneader, a roll, a monopodium extruder, a 2 shaft extruder, etc. To this invention constituent, other additives, for example, a chlorine-based compound, a bromine system compound, a plasticizer, lubricant, a stabilizer, an ultraviolet ray absorbent, a bulking agent, a coloring agent, a reinforcing agent, etc. can be added in the range which does not spoil the purpose of this invention.

[0025]

[Example] An example and the example of comparison are given to below, and this invention is explained to it. In addition, in the following examples and examples of comparison, many properties of the various styrene resins by which flameproofing was carried out were measured by the following method, and were evaluated.

(1) Izod impactive strength : by ASTM-D256, it measured using the test piece with a notch at 23 degrees C.

(2) BIKATTO softening temperature : it measured by ASTM-D1525.

(3) Fluidity : the melt flow rate was measured by ASTM-D1238.

(4) Flammability : U.S. undershirt rye TAZU laboratory in corporation (Underwriters.) Laboratories It was based on

the criteria of 94V-2 of the publication of 7-10 items of "the combustion test of the plastic material for parts of a UL94 safety-standard device" published from Inc. and U.S.A, 94V-1, and 94V-0 (it abbreviates to "V-2", "V-1", and "V-0" below.).

[0026]

[Examples 1-6] It is an ether derivative of a halogen content aromatic diol to the styrene-resin 100 weight section. Specified quantity mixture was carried out at the bromination bisphenol A epoxy resin (tradename EC14 molecular weight 1400 Dainippon Ink & Chemicals, Inc. make) and a rate which showed the bromination bibenzyl (made in tradename Saytex8010 Albemarle), and an antimony trioxide and a polytetrafluoroethylene (tradename F104 Daikin Industries, LTD. make) in Table 1 as a poly halogenation diphenyl alkane, with the biaxial extruder, after melting kneading (cylinder setting temperature of 200 degrees C), injection molding (200 degrees C of cylinder temperatures, 60 degrees C of die temperatures) was carried out, and the piece Izod impactive strength, BIKATTO softening temperature, a fluidity, lightfastness, and flammability were measured using this test piece, respectively. The result is shown in Table 1. However, the unit of the blending ratio of coal shown in the table is the weight section. Izod impactive strength, BIKATTO softening temperature, and a value with a melt flow rate satisfactory as a resin are shown, and flammability also has the fire retardancy ranked as V-0 of the purpose, and it has become the good thing of balance in total.

[0027]

[The examples 1 and 2 of comparison] The result which created the test piece in the same procedure as an example, and measured physical properties was shown in Table 2 except using by the ether derivative independent of a halogen content aromatic diol, or the poly halogenation diphenyl alkane independent, and not using the polytetrafluoroethylene. In the ether derivative independent case of a halogen content aromatic diol, an impact strength falls, and if fire retardancy is made to clear by the ether derivative independent of a halogen content aromatic [that a fluidity falls etc.] diol, or the poly halogenation diphenyl alkane independent when it is PORIHAROGENKA diphenyl alkane independent, it will become that toward which physical-properties balance inclined.

[0028]

[The examples 3 and 4 of comparison] Except not using poly tetrapod FUROORO ethylene, physical properties were measured with the same procedure as an example, and it was shown in Table 2. If the addition of a poly halogenation diphenyl alkane is made to increase until it has the fire retardancy ranked as V-0 made into the purpose, the Izod impactive strength and the fluidity which are made into the purpose will not be acquired.

[0029]

[The examples 5-8 of comparison] Physical properties were measured with the same procedure as an example, and it was shown in Table 2. If there are few additions of a polytetrafluoroethylene, it does not have the fire retardancy ranked as V-0 made into the purpose. Moreover, when there are many additions of a polytetrafluoroethylene, glow INGU after flame disappears is not subsided within convention time, and is not ranked as V-0 by the definition of UL94. Moreover, if there are few total amounts of a bromination bisphenol A epoxy resin and a bromination bibenzyl than the 12 sections, even if it will carry out optimum dose addition of the polytetrafluoroethylene, it cannot have the fire retardancy ranked as V-0. However, if there are more total amounts than the 21 sections, the physical properties as a resin cannot be maintained.

[0030]

[Table 1]

	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6
(A) スチレン系樹脂	100	100	100	100	100	100
(B) 臭素化ビスフェノールAエポキシ樹脂	2	8	14	18	8	8
(C) 臭素化ジフェニルエタン	10	9	4	3	9	9
(B) + (C)	12	17	18	21	17	17
(D) 三酸化アンチモン	5	5	5	5	5	5
(E) ポリテトラフルオロエチレン	0.05	0.05	0.05	0.05	0.01	0.5
アイゾット衝撃強度 (Kgc/cm)	10	7	7	6	7	7
ビカット軟化点 (°C)	103	100	97	96	100	100
メルトフローレイト (g/10min)	8	10	12	13	10	10
燃焼性 (1/8インチ)	V-0	V-0	V-0	V-0	V-0	V-0
グローイング	○	○	○	○	○	○

[0031]

[Table 2]

	比較例 1	比較例 2	比較例 3	比較例 4	比較例 5	比較例 6	比較例 7	比較例 8
(A) スチレン系樹脂	100	100	100	100	100	100	100	100
(B) 臭素化ビスフェノールAエポキシ樹脂	23		8	8	8	8	2	18
(C) 臭素化ジフェニルエタン		17	9	12	9	9	9	4
(B) + (C)	23	17	17	20	17	17	11	22
(D) 三酸化アンチモン	5	5	5	5	5	5	5	5
(E) ポリテトラフルオロエチレン					0.005	1	0.05	0.05
アイゾット衝撃強度 (Kgc/cm)	5	8	7	6	7	7	10	5
ビカット軟化点 (°C)	95	103	100	100	100	100	103	96
メルトフローレイト (g/10min)	15	4	10	8	10	9	8	13
燃焼性 (1/8インチ)	V-0	V-0	V-2	V-0	V-2	OUT	V-2	V-0
グローイング	○	○	○	○	○	×	○	○

[0032]

[Effect of the Invention] While it has the outstanding fire retardancy, it excels in thermal resistance, shock resistance, and fluid balance. Therefore, use effective in housing of home electronics, a business-machine machine, and information machines and equipment etc. is expected to the field and concrete target by which fire retardancy is demanded especially of the resin constituent of this invention.

[Translation done.]